

Chemistry

Lecture 15

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Chemical Kinetics/Reaction Kinetics

Outline:

- ✚ Rate of Reaction, Rate Equation, Rate Constant, Rate determining step
- ✚ Determination of Rate of chemical reaction
- ✚ Factors affecting Rate of reaction
- ✚ Units of Rate constant
- ✚ Order of reaction and its determination
- ✚ Activation energy and Activated complex

Reaction Kinetics

- ❖ Study of rates of chemical reactions and the factors that affect the rates of chemical reactions
- ❖ Microscopic property which deals with mechanism of reaction

Rate of Reaction (R):

- ❖ Change in concentration of a reactant or a product divided by the time taken for the change
- $$\text{Rate} = \frac{\text{change in conc. of substance}}{\text{time taken for change}} = \frac{\Delta C}{\Delta t}$$
- ❖ Unit is $\text{mol dm}^{-3} \text{s}^{-1}$
 - ❖ Rate of reaction decreases with time as concentration of reactant decreases

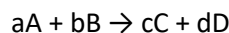
Instantaneous Rate (I.R)	Average Rate (A.R)
Rate at any one specific interval of time	Rate b/w two specific intervals of time
$I.R = \frac{dx}{dt}$	$A.R = \frac{\Delta C}{\Delta t}$
At first, I.R is higher than A.R	At the end, A.R is higher than I.R

Specific Rate Constant:

- Also called velocity constant (depends on nature of reaction)
- Specific rate constant of a chemical reaction is the rate of reaction when the concentrations of the reactants are unity
- $k = \frac{\text{Rate}}{[\text{Reactant}]}$ $\Rightarrow k = \text{rate}$
- Unit depends upon;
 - Order of reaction
 - Unit of time and unit of Conc.
- Its value remains constant under standard conditions
- Depends upon temperature

Rate Law/rate expression/rate equation:

- ❖ Gives relationship between rate of reaction and concentration of reactants
- ❖ It is determined experimentally



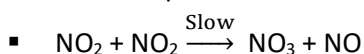
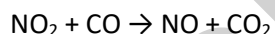
$$\text{Rate} = k [A]^a [B]^b$$

- ❖ Rate equation will give order of reaction too
- ❖ Gives mechanism of reaction

Rate Determining Step:

- If a reaction occurs in several steps, the slowest step whose rate determines rate of the overall rate of reaction is called rate determining step
- It can also give order of reaction (as gives rate equation)

For Example:



$$\text{Rate} = K [\text{NO}_2]^2$$

Factors affecting Rate of reaction:

1. Nature of Reactant:

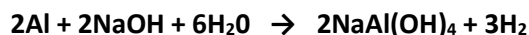
- IA elements react more faster with water than IIA elements
- Neutralization / ionic reactions/double decomposition reactions are very fast, whereas redox reactions are slow

2. Concentration of Reaction:

- Rate \propto Conc. of reactant (greater conc. means more collisions b/w particles)
- Combustion that occurs slowly in air (21 % oxygen) will occur more rapidly in pure oxygen
- Limestone reacts with different concentrations of hydrochloric acid at different rates.
- In the case of a gaseous reactant, its concentration can be increased by increasing its pressure
- Determines rate equation and order of reaction

3. Surface Area:

- Rate \propto Surface area (greater surface area means more collisions b/w particles)
- Al foil reacts with NaOH moderately when warmed, but powdered Al reacts rapidly with cold NaOH



- CaCO_3 in the powder form reacts with dilute H_2SO_4 more efficiently than its big pieces

4. Light:

- Rate \propto Light (light is source of energy)

- The reaction of CH_4 and Cl_2 requires light
- The reaction between H_2 and Cl_2 at ordinary pressure is negligible in darkness, slow in daylight, but explosive in sunlight
- Similarly, light is vital in photosynthesis

5. Temperature:

- Rate \propto Temperature (increase in 'T' increases K.E of molecules and thereby increasing the collisions b/w molecules)
- $10\text{ K} / 10^\circ\text{C}$ increase in 'T', doubles the rate of reaction

Methods to Determine Rate:

Physical Methods:

Comparatively more accurate and easy

i. Spectrometry:

- This method is applicable if a reactant or a product absorbs ultraviolet, visible or infrared radiation.
- The rate of reaction can be measured by measuring the amount of radiation absorbed
- Spectrophotometer is used

ii. Electrical Conductivity method:

- Involves ions which cause conductivity
- The conductivity of such a solution depends upon the rate of change of concentration of the reacting ions or the ions formed during the reaction
- The conductivity will be proportional to the rate of change in the concentration of such ions
- Electrical conductivity meter is used

iii. Dilatometric method:

- This method is useful for those reactions, which involve small volume changes in solutions
- The volume change is directly proportional to the extent of reaction
- Dilatometer is used

iv. Refractometric method:

- This method is applicable to reactions in solutions, where there are changes in refractive indices of the substances taking part in the chemical reactions
- Refractometer is used

v. Optical Rotation method:

- Angle through which plane polarized light is rotated by the reacting mixture is measured by a polarimeter
- The extent of rotation determines the concentration of optically active substance
- If any of the species in the reaction mixture is optically active, then this method can be followed to find out the rate of reaction

- Polarimeter is used

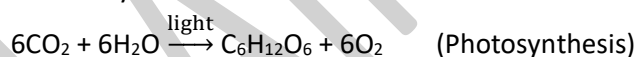
Chemical method:

- Comparatively less accurate and difficult to perform
- This is particularly suitable for reactions in solution. In this method, we do the chemical analysis of a reactant or a product
- Graph is plotted b/w time vs concentration and rate is determined from slope

Molecularity	Order of Reaction
No. of molecules involved in balanced chemical equation which result in formation of product	Sum of exponents of molar conc. of reactants as given in rate equation
Theoretical value	Experimental value
Molecularity not greater than 3	Can be 0,1,2,3
Can't be in fraction, zero and negative	Can be in fraction or negative
May or may not equal to order of reaction	Rate = $K [A]^m [B]^n$ Order = $m + n$

Zero Order Reaction:

- Rate of reaction is independent of conc. of any reactant
- Decomposition of ammonia [$2\text{NH}_3 \rightarrow \text{N}_2 + 3\text{H}_2$]
- Reaction b/w H_2 and Cl_2 in presence of sunlight is zero order
- Photochemical reactions usually are zero order



- Unit of K; $\text{mol dm}^{-3} \text{s}^{-1}$

1st Order Reaction:

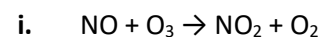
- Rate of reaction depends upon the conc. of only one reactant
 - Radioactive decay
 - $2\text{N}_2\text{O}_5 \rightarrow 2\text{N}_2\text{O}_4 + \text{O}_2$ Rate = $k [\text{N}_2\text{O}_5]$
 - $2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2$
 - $\text{NH}_4\text{NO}_2 \rightarrow 2\text{H}_2\text{O} + \text{N}_2$
- Unit of K; s^{-1}

Pseudo 1st Order Reaction:

- Rate of reaction depends upon the conc. of one reactant where the other reactant is in excess and does not affect rate of reaction
 - Hydrolysis of ester (water in excess)
 - Hydrolysis of cane sugar (water in excess)
 - Hydrolysis of tertiary butyl bromide
- Unit of K; s^{-1}

2nd Order Reaction:

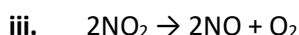
➤ **Unit of K; mol⁻¹dm³s⁻¹**



$$\text{Rate} = k [\text{NO}][\text{O}_3]$$



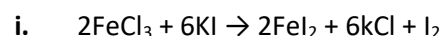
$$\text{Rate} = k [\text{NO}_2]^2$$



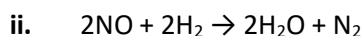
$$\text{Rate} = k [\text{NO}_2]^2$$

3rd Order Reaction:

➤ **Unit of K; mol⁻²dm⁶s⁻¹**

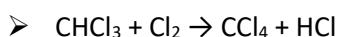


$$\text{Rate} = k [\text{FeCl}_3][\text{KI}]^2$$



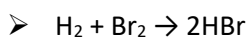
$$\text{Rate} = k [\text{NO}]^2[\text{H}_2]$$

Fractional Order Reaction:



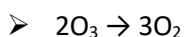
$$\text{Rate} = k [\text{CHCl}_3][\text{Cl}_2]^{1/2}$$

$$\text{Order} = 1.5$$



$$\text{Rate} = k [\text{H}_2][\text{Br}_2]^{1/2}$$

Negative Order Reaction:



$$\text{Rate} = k [\text{O}_3]^2[\text{O}_2]^{-1}$$

Rate decreases to half when concentration of oxygen doubles

Half life Period ($t_{1/2}$)

- Time required to convert 50% of the reactants into products
- N_2O_5 has half life of 24 minutes at 45°C
- ^{235}U has half life period of 710 million years

For 1st order reaction

$$(t_{1/2})_1 \propto \frac{1}{a^0}, (a=\text{conc.})$$

$$(t_{1/2})_1 = \frac{0.693}{k}$$

For 2nd order reaction

$$(t_{1/2})_2 \propto \frac{1}{a^1}, (a=\text{conc.})$$

$$(t_{1/2})_2 = \frac{1}{ka}$$

For 3rd order reaction

$$(t_{1/2})_3 \propto \frac{1}{a^2}, (a=\text{conc.})$$

$$(t_{1/2})_3 = \frac{1.5}{ka^2}$$

For nth order reaction

$$(t_{1/2})_n \propto \frac{1}{a^{n-1}}, (a=\text{conc.})$$

For zero order reaction

$$(t_{1/2})_0 \propto a$$

Determination of Order of Reaction:

- Method of hit and trial
- Graphical method
- Differential method
- Method of large excess (one of reactant is in small amount while other in excess)

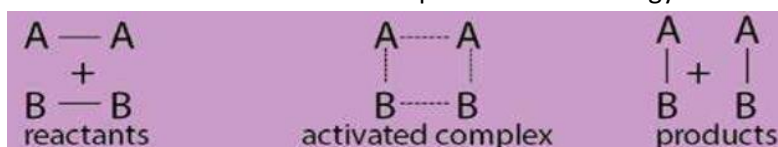
➤ Half life method
$$n = 1 + \frac{\log \left[\frac{t_1}{t_2} \right]}{\log \left[\frac{a_2}{a_1} \right]}$$

Activation Energy (E_a)

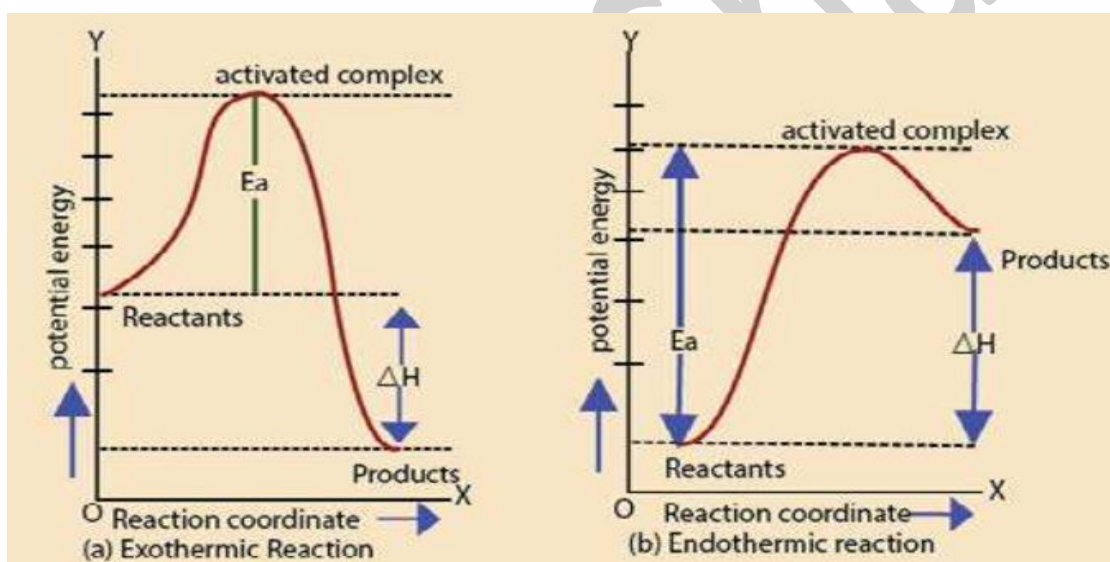
- ☞ The minimum amount of energy, required for an effective collision is called activation energy
- ☞ Depends on the chemical nature of reactants
- ☞ Affected by catalyst
- ☞ Explained with Collision theory and transition state theory

Collisions; Common molecular collisions are Bimolecular

- **Effective Collision:** Product forms, more effective collisions mean fast reaction
- **Ineffective Collision:** No product
- Molecules on collision form activated complex for which energy is maximum



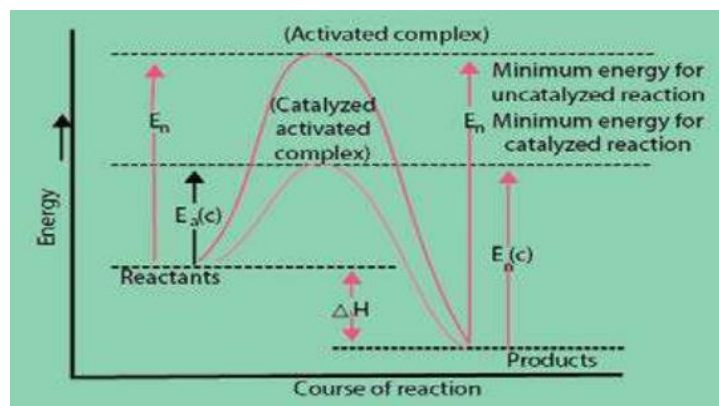
- ☞ It is a short lived species and decomposes into the products immediately.
- ☞ It has a transient existence, that is why it is also called a transition state



- ☞ E_a of exothermic reaction in forward direction is less than that of reverse
- ☞ E_a of endothermic reaction in forward direction is greater than that of reverse
- ☞ For exothermic; $\Delta H < E_a$
- ☞ For endothermic; $\Delta H > E_a$
- ☞ Can be calculated from solution of Arrhenius equation ($k = Ae^{-E_a/RT}$)
- ☞ Rate inversely related to E_a

Catalysis

- ◆ A substance that alters the rate of reaction but remains chemically unchanged at the end is called catalyst and process is called catalysis
- ◆ **Catalyst increases rate of reaction** by lowering activation energy
- ◆ Provides new path/mechanism



Homogenous Catalysis	Heterogeneous Catalysis
Reactants and catalyst are in same phase	Reactants and catalyst are in different phase
Reacting mixture is uniform throughout	Usually catalyst is solid on which gaseous reactants are adsorbed
$2\text{SO}_{2(g)} + \text{O}_{2(g)} \xrightleftharpoons{\text{NO}_{(g)}} 2\text{SO}_{3(g)}$	$4\text{NH}_{3(g)} + 5\text{O}_{2(g)} \xrightleftharpoons{\text{Pt}_{(s)}} 4\text{NO}_{(g)} + 6\text{H}_2\text{O}_{(l)}$
$\text{CH}_3\text{COOC}_2\text{H}_5_{(aq)} + \text{H}_2\text{O}_{(l)} \xrightleftharpoons{\text{H}_3\text{O}^+_{(aq)}} \text{CH}_3\text{COOH}_{(aq)} + \text{C}_2\text{H}_5\text{OH}_{(aq)}$	$\text{CH}_2=\text{CH}_{2(g)} + \text{H}_{2(g)} \xrightleftharpoons{\text{Ni}_{(s)}} \text{CH}_3-\text{CH}_{3(g)}$